

Quantum Confinement and Optical Gaps in Si Nanocrystals

Serdar Ögüt and James R. Chelikowsky

*Department of Chemical Engineering and Materials Science, Minnesota Supercomputer Institute,
University of Minnesota, Minneapolis, Minnesota 55455-0132*

Steven G. Louie

*Department of Physics, University of California at Berkeley, and Materials Science Division,
Lawrence Berkeley National Laboratory, Berkeley, California 94720*

(Received 20 May 1997)

Quasiparticle gaps, self-energy corrections, exciton Coulomb energies, and optical gaps in Si quantum dots are calculated from first principles using a real-space pseudopotential method. The calculations are performed on hydrogen-passivated spherical Si clusters with diameters up to 27.2 Å (~800 Si and H atoms). It is shown that (i) the self-energy correction in quantum dots is enhanced substantially compared to bulk, and is not size independent as implicitly assumed in all semiempirical calculations, and (ii) quantum confinement and reduced electronic screening result in appreciable excitonic Coulomb energies. Calculated optical gaps are in very good agreement with absorption data. [S0031-9007(97)03934-3]

PACS numbers: 78.66.Db, 61.46.+w, 71.35.Cc, 73.20.Dx

Optical properties of semiconductor quantum structures with reduced dimensions have been the subject of many experimental and theoretical studies. One of the motivations for these studies has been stimulated by the discovery of visible luminescence from porous Si [1]. Although there is still debate on the origin of photoluminescence, there is considerable experimental and theoretical evidence for the role of quantum confinement (QC) in producing this phenomenon [2]. However, the agreement among existing theoretical calculations with experimental absorption and photoluminescence data is fair, at best, with a common finding of an inverse correlation of the optical gap with the nanoparticle size. While this finding provides an important piece of evidence for QC models, a complete microscopic understanding of the size dependence of optical excitations in Si nanocrystals and porous Si is yet to be achieved. The aim of this Letter is to investigate the size dependence of optical gaps in Si nanocrystallites through large scale first principles calculations of quasiparticle gaps and exciton Coulomb energies, and to compare them with available calculations and experimental absorption data.

Almost all existing theoretical calculations on Si quantum dots are of a semiempirical nature [3–7]. Such an approach postulates the transferability of bulk electronic interaction parameters to the nanocrystalline environment. The validity of this assumption is not clear, and has been questioned in recent studies [8]. More specifically, QC-induced changes in self-energy corrections, which may affect the magnitude of the optical gaps significantly, are neglected in semiempirical calculations by implicitly assuming a “size-independent” correction which corresponds to that of the bulk. It naturally follows that a reliable way to investigate the optical gaps of quantum dots would be to perform *ab initio* calculations on these systems. However,

there have been two major bottlenecks for the application of first principles studies to quantum dots. First, accurate *ab initio* calculations have so far been limited, due to large computational demand, to small systems which usually do not correspond to the sizes of the nanoparticles for which experimental data are available. Second, even accurate *ab initio* calculations performed within the local density approximation (LDA) would suffer from the well-known underestimate of the band gap [9]. In order to remedy this problem, a few self-consistent density-functional-theory-based calculations within LDA have been performed where a size-independent self-energy correction of 0.68 eV (bulk limit) has been added [10]. This approach is, in principle, not so different from a semiempirical calculation, and does not address the effects of QC on the self-energy.

The first bottleneck, i.e., the large computational demand required in modeling quantum dots from first principles, can be overcome by straightforward application of new electronic structure algorithms, such as real-space methods [11,12], to these confined systems using massively parallel computational platforms. As for the second problem, i.e., the underestimate of the band gap due to LDA, while sophisticated formalisms like the GW approximation [9] would be quite accurate, the confined nature of the quantum dots makes it possible for a simpler formulation of the fundamental quasiparticle gaps. For an n -electron system, the quasiparticle gap $\varepsilon_g^{\text{qp}}$ can be expressed in terms of the ground state total energies E of the $(n + 1)$ -, $(n - 1)$ -, and n -electron systems as

$$\varepsilon_g^{\text{qp}} = E(n + 1) + E(n - 1) - 2E(n) \quad (1)$$

$$= \varepsilon_g^{\text{band}} + \Sigma, \quad (2)$$

where $\varepsilon_g^{\text{band}}$ is the usual single-particle LDA band gap (defined as the eigenvalue difference between the lowest

unoccupied and the highest occupied orbitals), and Σ is the self-energy correction. Therefore, the calculation of the quasiparticle gap requires the self-consistent solutions of three different charge configurations of each quantum dot. The computational demand of this approach can be reduced significantly by using the wave functions of the neutral cluster calculation to extract very good initial charge densities for the self-consistent calculations of the charged systems. With a real-space method, it is also quite straightforward to calculate the total energies for these charged systems [$E(n+1)$ and $E(n-1)$] without the use of a compensating background charge that would be necessary for a supercell geometry.

Our calculations were performed in real space using the higher-order finite-difference pseudopotential method [11]. Quantum dots were modeled by spherical bulk-terminated Si clusters that are passivated by hydrogen atoms at the boundaries. We used Troullier-Martins pseudopotentials [13] in nonlocal [14] and local forms for Si and H, respectively. All calculations were performed within LDA using the exchange-correlation functional of Ceperley and Alder as parametrized by Perdew and Zunger [15]. The kinetic energy in the finite-difference expression was expanded up to twelfth order in the grid spacing h , chosen to be 0.9 a.u. No change in the calculated gap values was found upon decreasing h to 0.75 a.u. The wave functions were required to vanish outside a spherical domain, which was at least 7.5 a.u. away from the last shell of Si atoms. The Hartree potential was solved by discretizing the Poisson equation and matching the boundary potential with that of a multipole expansion of the charge density with angular momentum $l = 9$ to 15 depending on the size of the system. All calculations were performed on a Cray C-90 computer, except for the two largest cases (Si₂₉₃H₁₇₂ and Si₅₂₅H₂₇₆), which were run in parallel on a Cray-T3E machine.

Size dependence of the quasiparticle and LDA band gaps, and self-energy corrections are shown in Fig. 1. Both gap values and self-energy corrections are enhanced substantially with respect to bulk values, and are inversely proportional to the dot diameter d as a result of QC. Specifically, $\epsilon_g^{\text{qp}}(d) - \epsilon_{g,\text{bulk}}^{\text{qp}}$, $\epsilon_g^{\text{band}}(d) - \epsilon_{g,\text{bulk}}^{\text{band}}$, and $\Sigma(d) - \Sigma_{\text{bulk}}$ scale as $d^{-1.2}$, $d^{-1.1}$, and $d^{-1.5}$, respectively. The quasiparticle gaps shown in Fig. 1 are significantly higher compared to the gap values obtained in earlier semiempirical calculations [3–6]. The main reason for this is the significant enhancement of electron self-energies due to QC, which cannot be properly taken into account in semiempirical approaches. The dotted horizontal line in Fig. 1 shows the self-energy correction to the LDA band gap in bulk Si, and it can be seen that even for a quantum dot with $d = 20$ Å, the self-energy correction is twice the bulk value of 0.68 eV.

For direct comparison with experimental absorption data, exciton Coulomb and exchange-correlation energies need to be included. Compared to the Coulomb energy, exciton exchange-correlation energies are much smaller

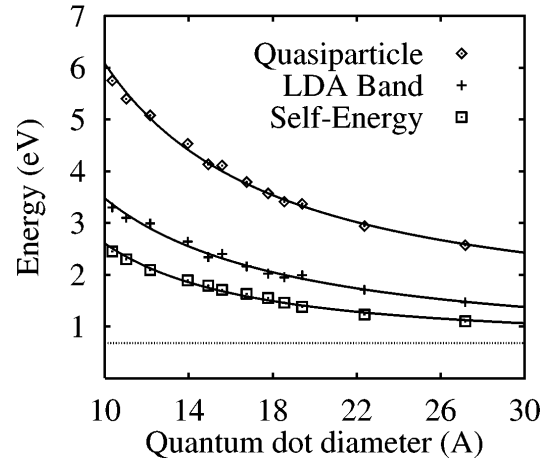


FIG. 1. Calculated quasiparticle (\diamond) and LDA band gaps ($+$), and self-energy corrections (\square) as a function of the quantum dot diameter d (in Å). The solid lines are power-law fits to the calculated data approaching the corresponding bulk limits. The horizontal dotted line is the bulk limit of the self-energy correction (0.68 eV).

for the quantum dots studied in this work, and will therefore be neglected. QC in nanostructures enhances the bare exciton Coulomb interaction, and also reduces electronic screening, so that the exciton Coulomb energy E_{Coul} can be comparable to the quasiparticle gap. Therefore, in order to extract the optical gaps, this term needs to be calculated accurately.

A crude, yet commonly used, approximation to E_{Coul} comes from the effective mass approximation (EMA), which assumes an infinite potential barrier at the boundary of the quantum dot and envelope wave functions for a noninteracting electron-hole pair in the form $\psi(\mathbf{r}) \sim \frac{1}{r} \sin(2\pi r/d)$. This approximation for E_{Coul} yields (in atomic units)

$$E_{\text{Coul}} = \frac{3.572}{\epsilon d}, \quad (3)$$

where ϵ is the dielectric constant of the quantum dot [16]. EMA, though commonly used, cannot be expected to yield accurate exciton Coulomb energies, since in this approximation the microscopic features of the electron-hole wave functions inside the quantum dot are neglected, and the wave functions are constrained to vanish abruptly outside the quantum dots, instead of decaying relatively slowly into the vacuum. We have, therefore, calculated E_{Coul} directly using *ab initio* pseudo-wave functions and the correct expression for this term, which can be written as

$$E_{\text{Coul}} = \int \frac{|\psi_e(\mathbf{r}_1)|^2 |\psi_h(\mathbf{r}_2)|^2}{\epsilon(\mathbf{r}_1, \mathbf{r}_2) |\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (4)$$

In this expression, ψ_e and ψ_h are the electron and hole wave functions, respectively, and $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$ is the microscopic screening dielectric response function. First, we set $\epsilon = 1$, and calculated the unscreened E_{Coul} . The results are shown in Fig. 2 along with the predictions of

the EMA and recent similar calculations of Francheschetti and Zunger [17] using semiempirical pseudopotentials. Our calculations for the unscreened exciton Coulomb energy are in quite good agreement with the semiempirical calculations of Ref. [17], both predicting *smaller* Coulomb energies and a softer power-law decay compared to EMA. Fitting the calculated data to a power law of the diameter as $d^{-\alpha}$, we find $\alpha = 0.7$, in good agreement with the semiempirical result of $\alpha = 0.8$. This figure also shows, as mentioned earlier, that the unscreened exciton Coulomb energies, although overestimated by the EMA, are comparable to the quasiparticle gaps. For example, for $\text{Si}_{293}\text{H}_{172}$ with $d = 22.4 \text{ \AA}$, the unscreened $E_{\text{Coul}} = 1.8 \text{ eV}$, while the calculated $\varepsilon_g^{\text{qp}} = 2.94 \text{ eV}$.

An accurate calculation of E_{Coul} in Eq. (4) requires the microscopic calculation of dielectric response function $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$. However, such a calculation for a quantum dot is quite cumbersome due to the large computational demand. Instead, we proceeded as follows: First, we calculated the polarizabilities of a few selected quantum dots using a finite-field method, and the static dielectric constants for these dots were obtained within the dielectric sphere model [18]. Next, we fitted the calculated static dielectric constants as a function of the quantum dot radius r to a generalized Penn model [19] to obtain $\epsilon(r) = 1 + (11.4 - 1)/[1 + (9.7/r)^{1.3}]$, where 11.4 is the bulk static dielectric constant of Si and r is measured in \AA . The fitting parameters to the generalized Penn model agree quite well with the parameters of Ref. [8]. Finally, we used this expression for $\epsilon(r)$ by approximating $\epsilon(\mathbf{r}_1, \mathbf{r}_2) \approx \epsilon(r = |\mathbf{r}_1 - \mathbf{r}_2|)$. We note that this formalism for the dielectric response function, while approximate, treats the effective screening more accurately in calculating E_{Coul} than using the static

dielectric constant of the quantum dot. In earlier studies, the dielectric response function $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$ was approximated by the static dielectric constant of either the bulk or the particular quantum dot [which corresponds to putting ϵ^{-1} outside the integral in Eq. (4)]. However, because of the wave-vector dependence of the dielectric function and QC, screening will have different effects at different length scales. For example, when \mathbf{r}_1 and \mathbf{r}_2 in Eq. (4) are very close to each other, there will be practically no screening, and $\epsilon \approx 1$. Since both the hole and electron wave functions are well localized towards the center of the quantum dot, the screening will be reduced significantly, resulting in larger Coulomb energies compared to the case of using a single dielectric constant for all distances.

The resulting optical gaps $\varepsilon_g^{\text{opt}} = \varepsilon_g^{\text{qp}} - E_{\text{Coul}}$ along with the quasiparticle gaps and experimental absorption data from Si nanocrystallites [20] are shown in Fig. 3. Although the calculated quasiparticle gaps are ~ 0.4 to 0.6 eV larger than the experimental absorption data, the calculated optical gaps are in excellent agreement with experiment. At this point, an interesting observation can be made about the good agreement of previous semiempirical calculations with experiment [2,3,5]. In the above semiempirical approaches, it is the underestimate of *both* the quasiparticle gaps *and* the exciton Coulomb energies (through the use of a static dielectric constant of either the bulk or the quantum dot), that puts the calculated values in good agreement with experiment. As a matter of fact, the bare gaps of Refs. [3] and [5] without the exciton Coulomb energies are in better agreement with the experiment. Our present results demonstrate that (i) the quasiparticle gaps in Si quantum dots are actually higher than previously thought, and (ii) the exciton Coulomb energies, because of the wave

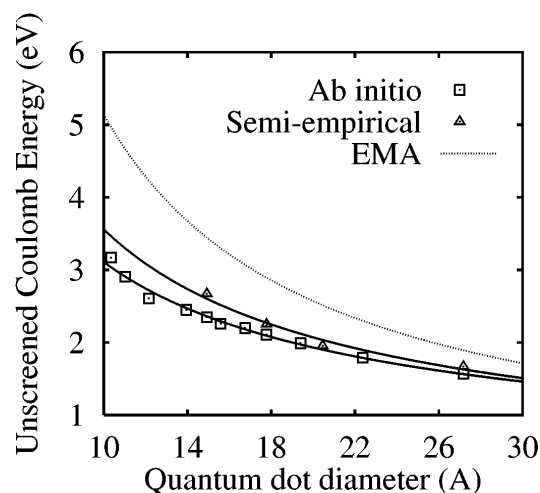


FIG. 2. Unscreened exciton Coulomb energies as a function of the quantum dot diameter d (in \AA) calculated by (i) effective mass approximation (dotted line), (ii) direct semiempirical pseudopotential calculations (\triangle from Ref. [17]), and (iii) direct *ab initio* pseudopotential calculations (\square) as explained in the text. The solid lines are power-law fits to the calculated data.

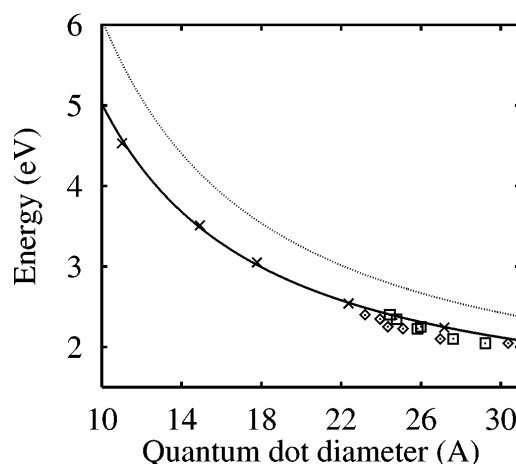


FIG. 3. Calculated quasiparticle gaps (dotted line), optical gaps (shown by \times fitted to the solid line), and experimental absorption data from Si nanocrystallites (\square and \diamond from Ref. [20]) as a function of the quantum dot diameter d (in \AA). The two sets of experimental data (\diamond and \square) differ by the method to estimate the nanocrystalline size.

vector dependence of the dielectric response function $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$, are higher than previously calculated, resulting in optical gap values that are in good agreement with the experimental absorption data.

In summary, we have implemented *ab initio* real-space calculations of quasiparticle and LDA band gaps, self-energy corrections, exciton Coulomb energies, and optical gaps for Si quantum dots with diameters up to 27.2 Å using the higher-order finite pseudopotential method. Our calculations indicate enhanced self-energy corrections compared to the bulk and substantial exciton Coulomb energies due to QC. Our calculated optical gaps are in very good agreement with the optical absorption data from Si nanocrystallites. Finally, we note that given the success of *ab initio* calculations for a better understanding of the optical absorption in Si nanocrystallites, further *ab initio* studies of luminescence in quantum dots, which will involve excited electronic states [21], are essential. Such studies are expected to help explain the large differences between absorption and luminescence energies [2] and the possible roles played by QC, surface states [22], and relaxations associated with Stokes shifts [23], towards a better microscopic understanding of visible luminescence from Si nanocrystals and porous Si.

We would like to thank J. Grossman and H. Kim for useful discussions and A. Stathopoulos, B. Rackner, and Y. Saad for their help in implementing the finite-difference pseudopotential code on the T3E. We also acknowledge support for this work by the National Science Foundation and Minnesota Supercomputer Institute. S.G.L. is supported by NSF DMR-9520554 and DOE DE-AC03-76SF00098.

-
- [1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
 - [2] D. J. Lockwood, Solid State Commun. **92**, 101 (1994).
 - [3] J. P. Proot, C. Delerue, and G. Allan, Appl. Phys. Lett. **61**, 1948 (1992); C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **48**, 11 024 (1993).
 - [4] T. Takagahara and K. Takeda, Phys. Rev. B **46**, 15 578 (1992).

- [5] L. W. Wang and A. Zunger, J. Phys. Chem. **98**, 2158 (1994).
- [6] N. A. Hill and K. B. Whaley, Phys. Rev. Lett. **75**, 1130 (1995); **76**, 3039 (1996).
- [7] C. Delerue, M. Lannoo, and G. Allan, Phys. Rev. Lett. **76**, 3038 (1996).
- [8] M. Lannoo, C. Delerue, and G. Allan, Phys. Rev. Lett. **74**, 3415 (1995); G. Allan, C. Delerue, M. Lannoo, and E. Martin, Phys. Rev. B **52**, 11 982 (1995).
- [9] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
- [10] B. Delley and E. F. Steigmeier, Phys. Rev. B **47**, 1397 (1993); Appl. Phys. Lett. **67**, 2370 (1995).
- [11] J. R. Chelikowsky, N. Troullier, and Y. Saad, Phys. Rev. Lett. **72**, 1240 (1994).
- [12] E. L. Briggs, D. J. Sullivan, and J. Bernholc, Phys. Rev. B **52**, R5471 (1995); F. Gygi and G. Galli, *ibid.* **52**, R2229 (1995); G. Zumbach, N. A. Modine, and E. Kaxiras, Solid State Commun. **99**, 57 (1996).
- [13] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
- [14] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
- [15] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [16] L. Brus, J. Phys. Chem. **90**, 2555 (1986); Y. Kayanuma, Phys. Rev. B **38**, 9797 (1988).
- [17] A. Francheschetti and A. Zunger, Phys. Rev. Lett. **78**, 915 (1997).
- [18] I. Vasiliev, S. Ögüt, and J. R. Chelikowsky, Phys. Rev. Lett. **78**, 4805 (1997).
- [19] R. Tsu and D. Babić, Appl. Phys. Lett. **64**, 1806 (1994); L. W. Wang and A. Zunger, Phys. Rev. Lett. **73**, 1039 (1994).
- [20] S. Furukawa and T. Miyasato, Phys. Rev. B **38**, 5726 (1988).
- [21] G. Allan, C. Delerue, and M. Lannoo, Phys. Rev. Lett. **76**, 2961 (1996).
- [22] F. Koch, V. Petrova-Koch, and T. Muschik, J. Lumin. **57**, 271 (1993).
- [23] E. Martin, C. Delerue, and M. Lannoo, Phys. Rev. B **50**, 18 258 (1994); T. Takagahara and K. Takeda, Phys. Rev. B **53**, R4205 (1996).